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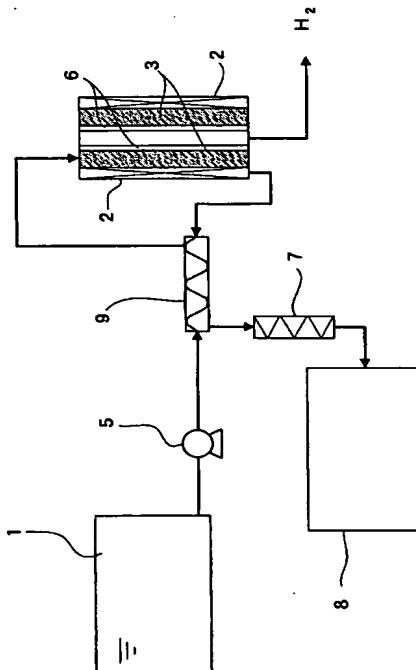
最終頁に続く

(54)【発明の名称】 燃料電池用水素燃料供給システム

(57)【要約】

【課題】水素製造効率が高く、しかもCO, CO₂を含まない液体水素化芳香族化合物を原料とする燃料電池用水素燃料供給システム及び供給方法を提供する。

【解決手段】常温で液体の水素化芳香族化合物原料貯蔵タンク、該液体水素化芳香族化合物を加熱器及び脱水素触媒を備えた脱水素触媒反応装置に供給する手段、触媒反応装置で得られる水素を分離する水素分離装置及び水素化芳香族化合物の脱水素生成物の冷却器及び脱水素生成物貯蔵タンクを備え、前記水素分離装置により分離された水素を燃料電池に供給する手段を備えた燃料電池用水素燃料供給システム



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【特許請求の範囲】

【請求項1】常温で液体の水素化芳香族化合物原料貯蔵タンク、該液体水素化芳香族化合物を加熱器及び脱水素触媒を備えた脱水素触媒反応装置に供給する手段、触媒反応装置で生成した水素を分離する水素分離装置及び水素化芳香族化合物の脱水素生成物の冷却器及び脱水素生成物貯蔵タンクを備え、前記水素分離装置により分離された水素を燃料電池に供給する手段を備えた燃料電池用水素燃料供給システム。

【請求項2】常温で液体の水素化芳香族化合物及び／又は芳香族化合物の貯蔵タンク、水素化芳香族化合物及び／又は芳香族化合物を触媒反応部及び冷却凝縮部を備えた脱水素触媒反応装置に供給する手段、脱水素触媒反応装置で生成した水素を分離する水素分離装置、及び脱水素生成物を前記貯蔵タンクに導く手段備え、前記水素分離装置により分離された水素を燃料電池に供給する手段を備えた燃料電池用水素燃料供給システム。

【請求項3】前記液体水素化芳香族化合物原料が、シクロヘキサン、メチルシクロヘキサン、ジメチルシクロヘキサン、1, 3, 5-トリメチルシクロヘキサンなどの单環式化合物またはデカルシン、メチルデカルシンなどの2環式化合物、または、テトラデカヒドロアントラゼンなどの3環式化合物である請求項1又は2に記載のシステム。

【請求項4】燃料電池への水素の供給圧力が0.1～3kgf/cm²である請求項1又は2に記載のシステム。

【請求項5】前記脱水素触媒が活性成分として白金、パラジウム、ルテニウム、ロジウム、イリジウム、ニッケル、コバルト、レニウム、バナジウム、タングステン、モリブデンからなる群から選ばれる少なくとも1種を含有し、触媒担体として、活性炭、ゼオライト、チタニア(TiO₂)、カーボンナノチューブ、モレキュラーシーブカーボン、ジルコニア(ZrO₂)、メソ細孔シリカ多孔質材料(FSM-16, MCM-41など)、アルミナ及びシリカからなる群から選ばれる少なくとも1種を含有する請求項1又は2に記載のシステム。

【請求項6】前記水素分離装置がAg-Pd膜、ゼオライト膜または多孔質シリカガラス膜である請求項1又は2に記載のシステム。

【請求項7】前記貯蔵タンクと前記脱水素触媒反応装置の間に熱交換器を設け、脱水素生成物を該熱交換器に通すことにより水素化芳香族化合物原料と脱水素生成物の熱交換を行う請求項1に記載のシステム。

【請求項8】前記脱水素触媒反応装置への水素の供給を可能にするバルブを更に設け、該バルブから水素を供給することにより、脱水素の逆反応が進行し、貯蔵タンク内の芳香族化合物を水素化芳香族化合物に変換可能とした請求項2に記載のシステム。

【請求項9】活性成分担持触媒において金属担持率が0.1～50%重量比であり、好ましくは0.5～10%重量比であ

る請求項1又は2に記載のシステム。

【請求項10】活性成分が白金触媒であり、添加活性成分Mの添加量がM/Pt原子比において0.1～10であり、好ましくは2～8である請求項1又は2に記載のシステム。

【請求項11】脱水素触媒反応の反応温度として50～350℃好ましくは80～250℃、反応圧力として0.1～10気圧、好ましくは1～5気圧である請求項1又は2に記載のシステム。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、燃料電池用水素燃料供給システムに関する。

【0002】また、本発明は自動車及び住宅用分散型燃料電池に適した水素吸蔵、供給システムに使用する単一連続型反応容器として用いられるベンゼン、トルエン、キシレン、メシチレンなどの單環芳香族化合物、ナフタレン、メチルナフタレンなどの2環芳香族化合物及びアントラゼンなどの3環芳香族化合物を水素添加し、水素吸蔵する際あるいは水素化物であるシクロヘキサン、メチルシクロヘキサン、ジメチルシクロヘキサンなどの单環水素化芳香族化合物、テトラリン、デカルシン、メチルデカルシンなどの2環水素化芳香族化合物、テトラデカヒドロアントラゼン、テトラデカヒドロメチルアントラゼンなどの3環水素化芳香族化合物を脱水素し、水素供給する際に使用する水素化及び脱水素システムに関する。

【0003】

【従来の技術】自動車並びに家庭用の燃料電池の水素燃料は、従来、圧縮水素、液体水素や水素ガス吸蔵材(合金、カーボンナノチューブ等)また、メタノールや炭化水素の水蒸気改質法により供給している。

【0004】しかしながら、圧縮水素、液体水素や水素ガス吸蔵材による水素供給は、大型な吸蔵装置が必要で、全体が極めて重くなる。また、充填時間が長くなるなどの課題がある。一方、メタノールなどの水蒸気改質法を利用する場合には改質触媒の耐久性に大きな課題がある。さらに、水蒸気改質法を利用する場合にはCOやCO₂が含まれるため、CO変成装置やCO₂分離装置などが必要であり、燃料電池装置が大型化する。

【0005】ベンゼンやナフタレンは水素化処理してシクロヘキサンとした後、酸化して樹脂原料として用いられ、またナフタレンは水素添加して各種塗料や溶剤として使用されるなど各種芳香族化合物はそのままでも用途は多いが水素添加して有効利用されることが多い。また水素添加した水素化芳香族化合物であるシクロヘキサン、メチルシクロヘキサン、ジメチルシクロヘキサンあるいはテトラリン、デカルシン、メチルデカルシンなどは脱水素反応により水素を発生し、相当する单環式又は2環式芳香族化合物に変換し、各種塗料や溶剤としてまた医薬、農薬、化成品の原料として用いられることが多い。

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芳香族化合物の水素化反応およびその相当する水素化芳香族化合物の脱水素反応は、通常触媒を用いて行われるが、従来から種々の物質が触媒として利用されており、ニッケル、白金、パラジウム、銅、クロム、ロジウム、ルテニウムなどの単一金属または2種以上の金属或いは金属酸化物、硫化物が単独或いは混合物として使用されている。これら金属はラネーニッケルや金属微粒子のように単独でも用いられるが表面積の大きな担体に担持させて用いることが多い。担体としてはシリカ、アルミニナ、活性炭、ゼオライトなどが用いられる。イオン交換法や含浸担持法などにより、金属を高分散状態でき、これを水素ガスやヒドラジンなどの還元剤を用いて還元すると高活性な芳香族化合物水素化及び脱水素触媒が得られる。

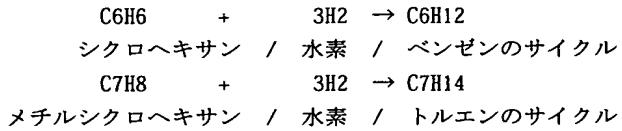
【0006】

【発明が解決しようとする課題】本発明の水素製造方法及び水素製造装置はこうした問題を解決し、常温で液体の芳香族化合物を水素吸蔵材として利用し、水素化芳香族化合物が高活性な脱水素触媒上で脱水素反応により、CO、CO₂を含まない高純度水素を発生するコンパクトな脱水素反応装置によって燃料電池用水素を製造・供給するシステムを提供することを目的とする。

【0007】

【課題を解決するための手段】本発明は、常温で液体の水素化芳香族化合物原料貯蔵タンク、該液体水素化芳香族化合物を加熱器及び脱水素触媒を備えた脱水素触媒反応装置に供給する手段、触媒反応装置で得られる水素を分離する水素分離装置及び水素化芳香族化合物の脱水素生成物の冷却器及び脱水素生成物貯蔵タンクを備え、前記水素分離装置により分離された水素を燃料電池に供給する手段を備えた燃料電池用水素燃料供給システム（以下、第1発明という）に関する。

【0008】また、本発明は、常温で液体の水素化芳香族化合物及び／又は芳香族化合物の貯蔵タンク、触媒反応部及び冷却凝縮部を備えた脱水素触媒反応装置、脱水素触媒反応装置で生成した水素を分離する水素分離装



3.燃料電池システムのコンパクト化ができる
液体水素化芳香族化合物原料としては、シクロヘキサン、メチルシクロヘキサン、ジメチルシクロヘキサン、1, 3, 5-トリメチルシクロヘキサンなどの单環式化合物またはデカリソ、メチルデカリソなどの2環式化合物、または、テトラデカヒドロアントラセンなどの3環式化合物が挙げられ、好ましくはシクロヘキサン、メチルシクロヘキサンである。

【0015】燃料電池への水素の供給圧力は、好ましくは0.1～3kgf/cm²である。

置、及び脱水素生成物を前記貯蔵タンクに導く手段備え、前記水素分離装置により分離された水素を燃料電池に供給する手段を備えた燃料電池用水素燃料供給システム（以下、第2発明という）に関する。

【0009】本発明のシステムは、自動車用及び家庭用のいずれにも使用することができる。

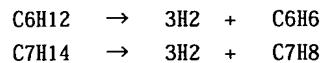
【0010】

【発明の実施の形態】第1発明及び第2発明について
本発明の特徴を以下に示す。

10 1.高純度水素を効率よく製造、供給することができる。
【0011】燃料電池では電極触媒に用いられる白金が、燃料電池に供給される水素（燃料水素）中に含まれるCOで被毒されるという問題があった。特に固体高分子型の燃料電池では、10ppm程度のCOで被毒される。本発明の燃料電池水素製造システム及び水素供給システムでは、固体高分子型の燃料電池を用いても、液体水素化芳香族化合物の脱水素反応であるため、水素のみを生成し、且つ水素のみを選択的に透過させる水素分離装置を備えるため、高純度の水素が燃料電池に供給されることにより、電極触媒の被毒問題を回避することができる。

20 2.シクロヘキサン、メチルシクロヘキサン、ジメチルシクロヘキサンなどの单環式化合物またはデカリソ、メチルデカリソなどの2環式化合物、または、テトラデカヒドロアントラセンなどの3環式化合物のような液体水素化芳香族化合物原料の脱水素により燃料電池水素燃料を供給するシステムを提供する。液体水素化芳香族化合物原料がシクロヘキサン、メチルシクロヘキサンの例を以下に示す。

【0013】



液体水素化芳香族化合物原料（例えばシクロヘキサン、メチルシクロヘキサン）のリサイクル使用ができる。

【0014】

【0016】前記脱水素触媒が活性成分は、白金、パラジウム、ルテニウム、ロジウム、イリジウム、ニッケル、コバルト、レニウム、バナジウム、タングステン、モリブデンからなる群から選ばれる少なくとも1種を含有する。触媒担体としては、活性炭、ゼオライト、チタニア(TiO₂)、カーボンナノチューブ、モレキュラーシークルカーボン、ジルコニア(ZrO₂)、メソ細孔シリカ多孔質材料(FSM-16, MCM-41など)、アルミナ及びシリカからなる群から選ばれる少なくとも1種を含有する。

50 【0017】水素分離装置としては、PdまたはPdとAgと

の合金膜 (Ag-Pd膜) 、ゼオライト膜または多孔質シリカガラス膜などの水素分離膜を好ましく使用できる。

【0018】活性成分担持触媒において金属担持率が0.1~50%重量比であり、好ましくは0.5~10%重量比である。

【0019】活性成分が白金触媒であり、添加活性成分Mの添加量がM/Pt原子比において0.1~10であり、好ましくは2~8であるのがより好ましい。

【0020】触媒活性成分の出発原料としては、特に限定されないが、金属の塩化物、硝酸塩、酢酸塩、アセチルアセトナート塩、カルボニル錯体またはシクロペニンニル錯体であるのが特に好ましい。

【0021】脱水素触媒反応の反応温度としては、特に限定されないが、50~350°C好ましくは80~250°C、反応圧力として0.1~10気圧、好ましくは1~5気圧であるのがよい。

【0022】触媒調製法として一般的に金属塩の水溶液、アルコール溶液或いは金属カルボニル錯体及びシクロペニニル錯体などの有機溶媒例えばシクロヘキサン、ベンゼン、トルエン、テトラヒドロフラン、ジエチルエーテルなどからの担体へ浸漬以外に、不活性ガス(窒素、アルゴン、ヘリウムなど)下で加熱、混合、CVD(化学蒸着法)により行われるが特に限定されるものでない。

第1発明について

本システムは燃料電池自動車や家庭発電用燃料電池に適用するにあたり、作動温度が低く、小型軽量である固体高分子型の燃料電池が好ましい。

【0023】貯蔵タンクと脱水素触媒反応装置の間に熱交換器を設け、脱水素生成物を該熱交換器に通すことにより水素化芳香族化合物原料と脱水素生成物の熱交換を行うのが好ましい。

【0024】図1に例示されるように、本第1発明のシステムは、常温で液体の水素化芳香族化合物原料貯蔵タンク1、該液体水素化芳香族化合物を加熱器2及び脱水素触媒3を備えた脱水素触媒反応装置4に供給する手段(ポンプ)5、触媒反応装置で得られる水素を分離する水素分離装置6及び水素化芳香族化合物の脱水素生成物の冷却器7及び脱水素生成物貯蔵タンク8を備え、好ましくは前記貯蔵タンクと前記脱水素触媒反応装置の間に熱交換器9を設け、脱水素生成物を該熱交換器に通すことにより水素化芳香族化合物原料と脱水素生成物の熱交換を行う。

【0025】貯蔵タンク1から供給される水素化芳香族化合物原料は、熱交換器において暖められ、脱水素触媒反応装置4に送られる。脱水素触媒反応装置4は加熱器2により50°Cから300°C程度、好ましくは80°Cから250°C程度に加熱されている。水素化芳香族化合物は該触媒装置4の脱水素触媒により脱水素され、芳香族化合物に変換される。該脱水素反応により生成した水素

は、水素分離装置6を通じて燃料電池に供給される。一方、脱水素反応生成物である芳香族化合物は、熱交換器9、冷却器7を通じて脱水素生成物貯蔵タンク8に送られる。

第2発明について

本発明は金属触媒を用いて図2に示された連続型単一反応容器内の多孔質材からなる触媒反応部Aに充填し、水素化芳香族化合物を含む単一の貯蔵タンクBを加熱器Jにより所定温度に加熱することにより、水素化芳香族化合物の沸点温度付近において蒸発し、加温蒸気は水素化芳香族化合物及び/又は芳香族化合物を加熱器及び脱水素触媒を備えた脱水素触媒反応装置Dに供給する手段である側面パイプEを通じて脱水素触媒反応装置Dに導入される。冷却凝縮部C(例えば10°C)において芳香族化合物及び/又は水素化芳香族化合物の蒸気が凝縮され、液滴として落下し、触媒反応部Aに滴下し、液膜を形成する。この液膜状態に於ける反応温度(180°C)において、水素化芳香族化合物は効率的に芳香族化合物に変換され水素を発生する。

【0026】液状になった芳香族化合物及び/又は水素化芳香族化合物は触媒反応部A内及び多孔質材(K)器壁を通過して液相を形成する。触媒反応部の触媒層と同じ位置(高さ)に接続された、脱水素生成物を前記貯蔵タンクに導く手段としての側面パイプFを通じて、液相芳香族化合物及び/又は水素化芳香族化合物はサイフォンの原理により単一の貯蔵タンクBに流れ込み、常に触媒層と同じ位置(高さ)を維持して芳香族化合物及び/又は水素化芳香族化合物の液面を形成し、触媒反応部に好ましい液膜が確保される。

【0027】冷却凝縮部Cの前後において気液分離が実現され、質量において軽くまた拡散運動の大きな水素ガスのみが上部パイプ水素分離装置Gを通じて出口バルブHを開くことにより高純度水素が分離精製されて、これにより住宅用及び自動車用燃料電池に効率よく水素が供給される。水素の貯蔵の際には、例えば住宅ないし自動車の外側部に取りつけられた半導体パネル板(アモルファスシリコン)を用いて太陽光の照射により発電した電力を制御して水の電気分解槽で発生した水素を導入するようになることができる。バルブHを閉じて、バルブIを開くことにより、高純度の水素ガスが触媒反応装置D内に導入される。所定温度に加熱された触媒反応部Aに充填した担持金属触媒により芳香族化合物は、効率的に水素化芳香族化合物に変換され、これにより水素の貯蔵がなされる。ベンゼンと変換されたシクロヘキサンの混合液は、側面パイプFのサイフォン効果により液膜状態を保持しつつ、貯蔵タンクBに回収され、貯蔵タンクBの芳香族化合物ないし水素化芳香族化合物は蒸発し、側面パイプFを通じて反応容器Dに導入される。冷却凝縮部Cにより冷却し凝縮され、芳香族化合物ないし水素化芳香族化合物は触媒反応部Aに入った触媒上に滴下

し、再び水素化反応が進行し、さらに水素化反応の転化率が向上する。これに芳香族化合物と水素化芳香族化合物の水素化反応および脱水素反応を連続して单一反応容器において実現され、水素の貯蔵・供給システムを提供することができる。

【0028】脱水素触媒反応装置への水素の供給を可能にするバルブを設けると、該バルブから水素を供給することにより、脱水素の逆反応が進行し、貯蔵タンク内の芳香族化合物を水素化芳香族化合物に変換可能となるので好ましい。

【0029】本システムは燃料電池自動車や家庭発電用燃料電池に適用するにあたり、作動温度が低く、小型軽量である固体高分子型の燃料電池が好ましい。

【0030】本発明者等は、上記発明の連続式单一反応容器を用いて、芳香族化合物の水素化および脱水素反応を利用した水素貯蔵および供給システムの効率的操業の最適化と触媒性能の改良を検討し、また連続型水素化・脱水素反応条件の探索を行った。

【0031】まず、触媒反応部Aの多孔質材からなる筒状容器Kの直径、高さおよび形状に制限されることはないが、多孔質（フィルター）材料の材質は、シリカ、アルミナ、活性炭纖維状など耐熱性と触媒層における芳香族化合物と水素化芳香族化合物の液膜形成が実現されるように外筒部との液の出入り、拡散等が最適化されることが好ましいことがわかった。

【0032】側面パイプEは、蒸気化に十分な加温、保温することが好ましい。側面パイプFは、比較的低温で芳香族化合物および水素化芳香族化合物の液柱が実現されるべく、設定されることが好ましい。冷却凝縮部Cは基本的には脱水素触媒反応装置Dの上部器壁を含む構造であるが、らせん状細管、交互冷却パイプ構造等、熱交換器を有するものあり、発生水素との芳香族化合物および水素化芳香族化合物との気液分離を効率的に実現すること、また触媒反応部Aにおける触媒層の液膜状態を維持するために最適温度の冷却水（例えば5～20℃）を調節して実施することが好ましい。

【0033】水素の分離、精製の操作手段は、実質的には冷却凝縮部Cの接触面積、冷却水温度、発生水素温度等の諸因子を考慮することにより可能であるが、さらに、高純度（99.9%）以上の高純度水素の供給が必要の場合には、シリカ分離膜やパラジウム・銀分離膜等従来技術による水素分離装置Gを設置することにより実現される。芳香族化合物および/または水素化芳香族化合物の貯蔵部Bは基本的にはそれらの沸点付近に設定し、比較的には触媒反応部Aより低温に設定されることが一般的であるが、この限りではない。水素貯蔵のプロセスにおける芳香族化合物の水素化反応は一般的には常圧～10気圧で行われることが多いが、この限りではない。

【0034】住宅用及び自動車用の水素貯蔵および供給

の効率を向上させるため触媒として用いられる担持金属触媒の検討を行った。一般的に貴金属触媒、例えば炭素担持白金触媒が芳香族化合物の水素化反応および脱水素反応に有効であるが、最近これにイリジウム、ルテニウム、レニウム、モリブデン、タンゲステン等の金属塩を添加し水素還元処理を行うと触媒性能が向上すること、また金属材料として担持するカルボニル錯体やアセチルアセトナート塩、シクロペンタジエニル錯体等を同時あるいは逐次的に主触媒金属である炭素担持白金触媒に添加し、加熱分解後水素還元処理を行うことにより、さらに水素貯蔵および水素供給効率が改善されることがわかった。

【0035】

【発明の効果】第1発明のシステムによれば、高純度の水素を容易に燃料電池に供給することができる。

【0036】第2発明の連続型单一反応容器を用いて高性能の金属触媒の存在下芳香族化合物の水素化反応および脱水素反応を効率的に進行せしめることができ、水素の貯蔵および供給を連続的に且つ单一反応容器において実現することができる、これにより自動車および家庭発電用固体燃料電池水素貯蔵・供給システムを長時間良好な状態で維持できる。

【0037】

【実施例】以下、本発明を実施例及び比較例を用いてより詳細に説明する。

実施例1

塩化白金酸3.3gを水溶液を用いてメゾ細孔多孔質材（FSM-16、 $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.00$ 、細孔径27.5Å）、表面積970m²/g) 30gに浸漬し、110℃で24時間蒸発乾固したあと、320℃で真空排気を2時間行い、5%白金活性成分(1)を調製した。この触媒を用いて、次の要領でシクロヘキサンの脱水素反応を行い、シクロヘキサンの転化率と水素発生速度を測定した。触媒を触媒反応部Aに充填し、水素気流中300℃にて1時間還元した。

【0038】27m¹シクロヘキサンを貯蔵部Bに入れ反応容器内を高純度アルゴンで置換したあと、貯蔵部Bを90℃に加温し、触媒反応部Aを180℃に加温し、また冷却凝縮部Cを10℃に水冷（ポンプ）したところ、20分後から水素生成が開始し、1時間30分後の初期水素生成速度は毎時12.0Lであり、シクロヘキサンのベンゼンへの転化率は25%であった。

【0039】また、シクロヘキサンの代わりにベンゼン27m¹を貯蔵部Bに入れ、触媒反応部Aに触媒（1）、同様に水素気流で300℃2時間還元後、反応温度200℃、1気圧水素下、ベンゼンの水素化反応を行った。反応生成物は、シクロヘキサンのみであった。またベンゼン初期転化率18%、5時間後52%であった。

50 比較例1

反応容器として、従来型固定床気相流通式反応装置（内径1.8cmのSUS製反応器に触媒Aを充填）を用いて、シクロヘキサン蒸気圧（90°C）を流通して反応温度180°Cで行った。SV=1500ml/gcat/水素生成速度は毎時0.8Lでシクロヘキサン転化率は1.6%であった。一部シクロヘキサンの分解物であるメタン、n-ヘキサン、プロパン、エタンが少量検出された。

比較例2

反応容器として従来型静置式オートクレーブ（SUS製箱状容器、容積150ml）に触媒Aを30g充填し、H₂下250°C還元2hを行った後、シクロヘキサンを導入し、180°Cに加熱し反応を行った。懸濁状態で内部攪拌を行いながら180°Cで反応生成物の分析を行った。水素の生成速度は0.35mlであり、シクロヘキサンの転化率は0.85%であった。

実施例2

塩化白金酸3.3gの水溶液を用いて活性炭3200m²/g、アルカリ処理）に浸漬したあと、空气中110°Cで15時間乾燥した。H₂気流中で350°Cで還元して5%活性炭担持触媒Bを得た。この触媒BとIr₄(CO)₁₂、Mo(CO)₆、Ru₃(CO)₁₂、Re₂

シクロヘキサン脱水素反応での水素生成活性

触媒	M/Pt	水素生成速度 (L/h)	シクロヘキサン 転化率(%)
Pt/C	0	16.0	20
Pt-Ir/C	5	46.4	58
Pt-Re/C	3	22.4	28
Pt-Mo/C	4	28.0	35
Pt-W/C	5	36.0	45
Pt-Ru/C	8	20.0	25

【0041】

【表2】

デカリン脱水素反応での水素生成活性

触媒	M/Pt	水素生成速度 (L/h)	シクロヘキサン 転化率(%)
Pt/C	0	3.8	18
Pt-Re/C	3	4.6	22
Pt-Ru/C	8	4.2	20
Pt-W/C	5	5.7	27
Pt-Ir/C	4	7.7	36

【図面の簡単な説明】

【図1】第1発明の装置の概略図である。

【図2】第2発明の装置の概略図である。

【符号の説明】

1 水素化芳香族化合物原料貯蔵タンク

2 加熱器

3 脱水素触媒

50 4 脱水素触媒反応装置

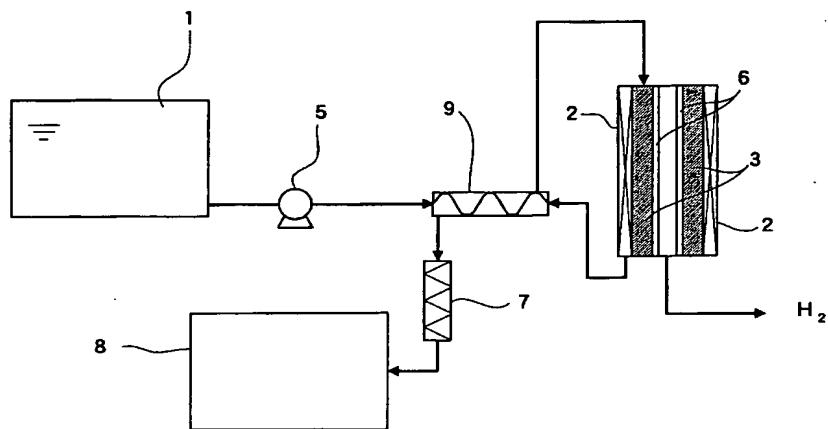
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5 液体水素化芳香族化合物の供給手段（ポンプ）
 6 水素分離装置
 7 冷却器
 8 脱水素生成物貯蔵タンク
 9 热交換器
 A 触媒反応部
 B 水素化芳香族化合物及び／又は芳香族化合物の貯蔵
 タンク
 C 冷却凝縮部

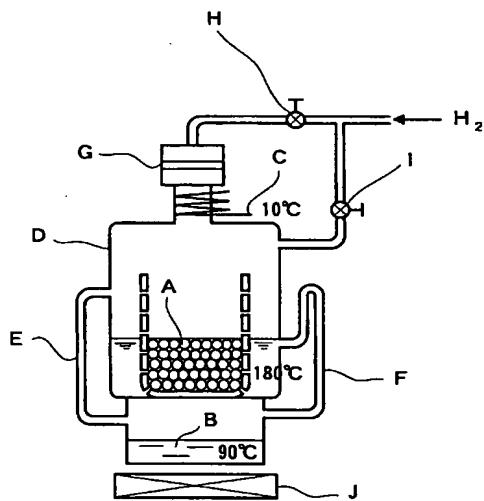
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D 脱水素触媒反応装置
 E 側面パイプ
 F 側面パイプ
 G 水素分離装置
 H 出口バルブ
 I バルブ
 J 加熱器
 K 多孔質材容器

【図1】



【図2】



フロントページの続き

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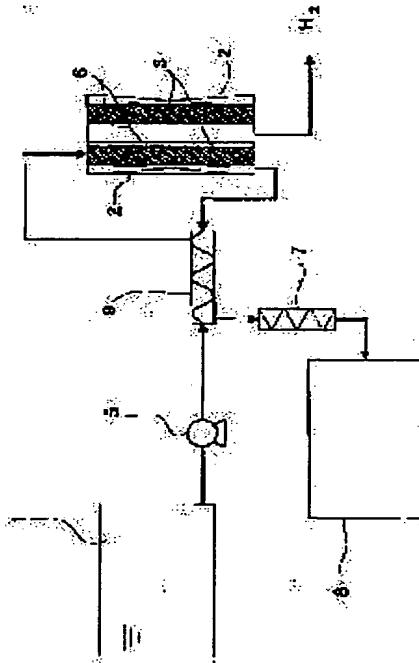
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(54) HYDROGEN FUEL SUPPLY SYSTEM FOR FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrogen fuel supply system for a fuel cell and a supplying method of hydrogen fuel, where a material of fuel cell is liquid hydrogenated aromatic compound which does not contain carbon monoxide and carbon dioxide and has high hydrogen production efficiency.

SOLUTION: A hydrogen fuel supply system for a fuel cell comprises a hydrogenated aromatic compound material storage tank, where hydrogenated aromatic compound is in a liquid condition at normal temperature, means for supplying liquid hydrogenated aromatic compound to a dehydrogenation catalysis reaction apparatus equipped with a heater and a dehydrogenation catalyst, and means for supplying hydrogen isolated by a hydrogen isolation equipment to the fuel cell comprising the hydrogen isolation equipment for isolating hydrogen that is generated by the catalysis reaction apparatus, a cooling equipment for cooling dehydrogenated products of hydrogenated aromatic compound, and a dehydrogenated products storage tank.



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CLAIMS

[Claim(s)]

[Claim 1] The hydrogen fuel distribution system for fuel cells which was equipped with the condensator and dehydrogenation product storage tank of a dehydrogenation product of a means to supply the dehydrogenation catalyst reactor equipped with the heater and the dehydrogenation catalyst for the hydrogenation aromatic compound raw material storage tank of a liquid, and this liquid hydrogen-ized aromatic compound, the hydrogen decollator which separates the hydrogen which generated with catalytic-reaction equipment, and a hydrogenation aromatic compound in ordinary temperature, and was equipped with a means supply the hydrogen separated by said hydrogen decollator to a fuel cell.

[Claim 2] The hydrogen fuel distribution system for fuel cells equipped with a means to supply the hydrogen decollator which separates a means to supply the dehydrogenation catalyst reactor equipped with the catalytic-reaction section and the cooling condensation section for the storage tank of the hydrogenation aromatic compound of a liquid, and/or an aromatic compound, the hydrogenation aromatic compound, and/or the aromatic compound, and the hydrogen which generated with the dehydrogenation catalyst reactor in ordinary temperature and the means preparation which leads a dehydrogenation product to said storage tank, and the hydrogen separated by said hydrogen decollator to a fuel cell.

[Claim 3] The system according to claim 1 or 2 said whose liquid hydrogen-ized aromatic compound raw materials are three cyclic compounds, such as two cyclic compounds, such as monocyclic compounds, such as a cyclohexane, a methylcyclohexane, dimethylcyclohexane, 1 and 3, and a 5-trimethyl cyclohexane, or a decalin, and a methyl decalin, or a tetra-deca hydronium anthracene.

[Claim 4] The system according to claim 1 or 2 whose supply pressure of the hydrogen to a fuel cell is 0.1 - 3 kgf/cm².

[Claim 5] Said dehydrogenation catalyst as an active ingredient Platinum, palladium, a ruthenium, a rhodium, At least one sort chosen from the group which consists of iridium, nickel, cobalt, a rhenium, vanadium, a tungsten, and molybdenum is contained. As catalyst support Activated carbon, a zeolite, a titania (TiO₂), a carbon nanotube, The system containing at least one sort chosen from the group which consists of molecular-sieve carbon, a zirconia (ZrO₂), meso pore silica porous materials (FSM-16, MCM-41, etc.), an alumina, and a silica according to claim 1 or 2.

[Claim 6] The system according to claim 1 or 2 said whose hydrogen decollator is the Ag-Pd film, the zeolite film, or the porosity silica glass film.

[Claim 7] The system according to claim 1 which performs heat exchange of a hydrogenation aromatic compound raw material and a dehydrogenation product by preparing a heat exchanger between said storage tanks and said dehydrogenation catalyst reactors, and letting a dehydrogenation product pass to this heat exchanger.

[Claim 8] The system according to claim 2 which the reverse reaction of a dehydrogenation advanced and enabled conversion of the aromatic compound in a storage tank to a hydrogenation aromatic compound by preparing further the bulb which enables supply of the hydrogen to said dehydrogenation catalyst reactor, and supplying hydrogen from this bulb.

[Claim 9] It is the system according to claim 1 or 2 which the rate of metal support is 0.1 - 50% weight ratio in an active-ingredient support catalyst, and is 0.5 - 10% weight ratio preferably.

[Claim 10] It is the system according to claim 1 or 2 which an active ingredient is a platinum catalyst, and the additions of the addition active ingredient M are 0.1-10 in a M/Pt atomic ratio, and are 2-8 preferably.

[Claim 11] They are 80-250 degrees C and the system according to claim 1 or 2 which is one to 5 atmospheric pressure preferably 0.1 to 10 atmospheric pressure as reaction pressure preferably 50-350 degrees C as reaction temperature of a dehydrogenation catalyst reaction.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to the hydrogen fuel distribution system for fuel cells. [0002] Moreover, the hydrogen absorption to which this invention was suitable for the automobile and the dispersion fuel cell for residences, The benzene used as a single linkage mold reaction container used for a distribution system, Monocyclic aromatic compound compounds, such as toluene, a xylene, and a mesitylene, naphthalene, 3 ring aromatic compounds, such as 2 ring aromatic compounds, such as a methylnaphthalene, and an anthracene, are hydrogenated. The cyclohexane, methylcyclohexane which are a hydride in case hydrogen absorption is carried out, Monocycle hydrogenation aromatic compounds, such as dimethylcyclohexane, a tetralin, It is related with hydrogenation and the dehydrogenation system which carry out the dehydrogenation of the 3 ring hydrogenation aromatic compounds, such as 2 ring hydrogenation aromatic compounds, such as a decalin and a methyl decalin, a tetra-deca hydronalium anthracene, and a TETORADEKA hydronalium methyl anthracene, and are used in case hydrogen supply is carried out.

[0003]

[Description of the Prior Art] the hydrogen fuel of the fuel cell of home use [list / automobile] -- former and compression hydrogen, liquid hydrogen, and hydrogen gas occlusion material (an alloy, carbon nanotube, etc.) -- it supplies with the steam reforming process of a methanol or a hydrocarbon again. [0004] However, large-sized occlusion equipment is required for the hydrogen supply by compression hydrogen, liquid hydrogen, or hydrogen gas occlusion material, and the whole becomes very heavy. Moreover, technical problems, like an injection time becomes long occur. On the other hand, in using the steam reforming process of a methanol etc., a big technical problem is in the endurance of a reforming catalyst. Furthermore, since CO and CO₂ are contained when using a steam reforming process, CO potential device, CO₂ decollator, etc. are required, and fuel cell equipment is enlarged.

[0005] After carrying out the hydrogen treating of benzene or the naphthalene and considering as a cyclohexane, it oxidizes and is used as a resin raw material, and naphthalene is hydrogenated, even when various aromatic compounds, such as being used as various coatings or a solvent, remain as they are, it hydrogenates and an application is used effectively in many cases, although many. Moreover, the cyclohexane which is the hydrogenated hydrogenation aromatic compound, a methylcyclohexane, dimethylcyclohexane or a tetralin, a decalin, a methyl decalin, etc. generate hydrogen by dehydrogenation, change it into a corresponding monocycle type or corresponding 2 ring type aromatic compound, and are used as physic, agricultural chemicals, and a raw material of a coal chemical product as various coatings or a solvent again in many cases. Various matter is used as a catalyst from the former, and the hydrogenation reaction of an aromatic compound and its corresponding dehydrogenation of a hydrogenation aromatic compound are used as that single metals, such as nickel, platinum, palladium, copper, chromium, a rhodium, and a ruthenium, two or more sorts of metals or a metallic oxide, and a sulfide are independent, or mixture, although usually carried out using a catalyst. Although it is used even when it is independent like a Raney nickel catalyst metallurgy group particle, support with big surface area is made to support these metals, and they are used in many cases. A silica, an alumina, activated carbon, a zeolite, etc. are used as support. if the high distribution condition of the metal can be carried out and this is returned by the ion-exchange method, the sinking-in supporting method, etc. using reducing agents, such as hydrogen gas and a hydrazine, -- high -- activity aromatic compound hydrogenation and dehydrogenation catalyst are acquired.

[0006]

[Problem(s) to be Solved by the Invention] the hydrogen manufacture approach and hydrogen

manufacturing installation of this invention -- such a problem -- solving -- ordinary temperature -- the aromatic compound of a liquid -- as hydrogen absorption material -- using -- a hydrogenation aromatic compound -- high -- it aims at offering the system which manufactures and supplies the hydrogen for fuel cells with the compact dehydrogenation equipment which generates the high grade hydrogen which does not contain CO and CO₂ by dehydrogenation on an activity dehydrogenation catalyst.

[0007]

[Means for Solving the Problem] A means by which this invention supplies the hydrogenation aromatic compound raw material storage tank of a liquid, and this liquid hydrogen-ized aromatic compound to the dehydrogenation catalyst reactor equipped with the heater and the dehydrogenation catalyst in ordinary temperature, It has the condensator and dehydrogenation product storage tank of a dehydrogenation product of the hydrogen decollator which separates the hydrogen obtained with catalytic-reaction equipment, and a hydrogenation aromatic compound. It is related with the hydrogen fuel distribution system for fuel cells equipped with a means to supply the hydrogen separated by said hydrogen decollator to a fuel cell (henceforth the 1st invention).

[0008] Moreover, this invention relates to the hydrogen fuel distribution system for fuel cells equipped with a means to supply the dehydrogenation catalyst reactor equipped with the storage tank of the hydrogenation aromatic compound of a liquid, and/or an aromatic compound, the catalytic-reaction section, and the cooling condensation section in ordinary temperature, the hydrogen decollator which separates the hydrogen generated with the dehydrogenation catalyst reactor and the means preparation which leads a dehydrogenation product to said storage tank, and the hydrogen separated by said hydrogen decollator to a fuel cell (henceforth the 2nd invention).

[0009] The system of this invention can be used for both the object for automobiles, and home use.

[0010]

[Embodiment of the Invention] The description of this invention is shown below about the 1st invention and the 2nd invention.

1. High grade hydrogen can be manufactured and supplied efficiently.

[0011] In a fuel cell, there was a problem that poisoning of the platinum used for an electrode catalyst was carried out by CO contained in the hydrogen (fuel hydrogen) supplied to a fuel cell. With the fuel cell of a solid-state macromolecule mold, poisoning is especially carried out by about 10 ppm CO. In the fuel cell hydrogen manufacturing system and hydrogen distribution system of this invention, since it has the hydrogen decollator which only hydrogen is generated [decollator] and makes only hydrogen penetrate alternatively since it is the dehydrogenation of a liquid hydrogen-ized aromatic compound even if it uses the fuel cell of a solid-state macromolecule mold, the poisoning problem of an electrode catalyst is avoidable by supplying the hydrogen of a high grade to a fuel cell.

[0012] In addition, as a fuel cell, a polymer electrolyte fuel cell is desirable. 2. Offer the system which supplies fuel cell hydrogen fuel according to the dehydrogenation of a liquid hydrogen-ized aromatic compound raw material like three cyclic compounds, such as two cyclic compounds, such as monocyclic compounds, such as a cyclohexane, a methylcyclohexane, dimethylcyclohexane, 1 and 3, and a 5-trimethyl cyclohexane, or a decalin, and a methyl decalin, or a tetra-deca hydronalium anthracene. A liquid hydrogen-ized aromatic compound raw material shows the example of a cyclohexane and a methylcyclohexane below.

[0013]

C₆H₁₂ -> 3H₂ + C₆H₆C₇H₁₄ -> 3H₂ + Recycle use of a C₇H₈ liquid-hydrogen-ized aromatic compound raw material (for example, a cyclohexane, a methylcyclohexane) can be performed.

[0014]

C₆H₆ + 3H₂ -> C₆H₁₂ Cyclohexane / Hydrogen / The cycle of benzene C₇H₈ + 3H₂ -> C₇H₁₄ methylcyclohexane / Hydrogen / As a liquid hydrogen-ized aromatic compound raw material which can perform miniaturization of the cycle 3. fuel cell system of toluene A cyclohexane, a methylcyclohexane, dimethylcyclohexane, Three cyclic compounds, such as two cyclic compounds, such as monocyclic compounds, such as a 1, 3, and 5-trimethyl cyclohexane, or a decalin, and a methyl decalin, or a tetra-deca hydronalium anthracene, are mentioned, and they are a cyclohexane and a methylcyclohexane preferably.

[0015] The supply pressure of the hydrogen to a fuel cell is 0.1 - 3 kgf/cm² preferably.

[0016] At least one sort as which said dehydrogenation catalyst is chosen from the group which an active ingredient becomes from platinum, palladium, a ruthenium, a rhodium, iridium, nickel, cobalt, a rhenium, vanadium, a tungsten, and molybdenum is contained. As catalyst support, at least one sort chosen from the group which consists of activated carbon, a zeolite, a titania (TiO₂), a carbon nanotube, molecular-sieve

carbon, a zirconia (ZrO_2), a meso pore silica porous material, an alumina, and a silica is contained (FSM-16, MCM-41, etc.).

[0017] As a hydrogen decollator, hydrogen demarcation membranes, such as Pd or alloy film (Ag-Pd film) of Pd and Ag, zeolite film, or porosity silica glass film, can be used preferably.

[0018] In an active-ingredient support catalyst, the rate of metal support is 0.1 - 50% weight ratio, and it is 0.5 - 10% weight ratio preferably.

[0019] An active ingredient is a platinum catalyst, the additions of the addition active ingredient M are 0.1-10 in a M/Pt atomic ratio, and it is more desirable that it is 2-8 preferably.

[0020] Especially as a start raw material of a catalytic activity component, although not limited, it is desirable that it is especially a chloride, a nitrate, acetate, an acetylacetone salt, a metaled carbonyl complex, or a metaled cyclopentane nil complex.

[0021] Especially as reaction temperature of a dehydrogenation catalyst reaction, although not limited, it is preferably good as 80-250 degrees C and reaction pressure that it is [50-350-degree C] one to 5 atmospheric pressure preferably 0.1 to 10 atmospheric pressure.

[0022] As the catalyst method of preparation, generally, from organic solvents, for example, a cyclohexane, such as a water solution of a metal salt, an alcoholic solution or a metal-carbonyl complex, and a cyclo pen TANIRU complex, benzene, toluene, a tetrahydrofuran, diethylether, etc. to support, especially although carried out by heating, mixing, and CVD (chemical vapor deposition) under inert gas (nitrogen, an argon, helium, etc.) in addition to immersion, it is not limited.

In applying this system to a fuel cell powered vehicle or the fuel cell for a home generation of electrical energy about the 1st invention, operating temperature is low and the fuel cell of the solid-state macromolecule mold which is a small light weight is desirable.

[0023] It is desirable by preparing a heat exchanger between a storage tank and a dehydrogenation catalyst reactor, and letting a dehydrogenation product pass to this heat exchanger to perform heat exchange of a hydrogenation aromatic compound raw material and a dehydrogenation product.

[0024] So that it may be illustrated by drawing 1 the system of **** 1 invention A means (pump) 5 to supply the hydrogenation aromatic compound raw material storage tank 1 of a liquid, and this liquid hydrogen-ized aromatic compound to the dehydrogenation catalyst reactor 4 equipped with the heater 2 and the dehydrogenation catalyst 3 in ordinary temperature, the hydrogen decollator 6 which separates the hydrogen obtained with catalytic-reaction equipment And it has the condensator 7 and the dehydrogenation product storage tank 8 of a dehydrogenation product of a hydrogenation aromatic compound. A heat exchanger 9 is preferably formed between said storage tanks and said dehydrogenation catalyst reactors, and heat exchange of a hydrogenation aromatic compound raw material and a dehydrogenation product is performed by letting a dehydrogenation product pass to this heat exchanger.

[0025] The hydrogenation aromatic compound raw material supplied from a storage tank 1 is warmed in a heat exchanger, and is sent to the dehydrogenation catalyst reactor 4. About 300 degrees C of dehydrogenation catalyst reactors 4 are preferably heated from 50 degrees C from 80 degrees C to about 250 degrees C by the heater 2. The dehydrogenation of the hydrogenation aromatic compound is carried out by the dehydrogenation catalyst of this catalyst equipment 4, and it is changed into an aromatic compound. The hydrogen generated by this dehydrogenation is supplied to a fuel cell through the hydrogen decollator 6. On the other hand, the aromatic compound which is a dehydrogenation product is sent to the dehydrogenation product storage tank 8 through a heat exchanger 9 and a condensator 7.

By filling up with this invention the catalytic-reaction section A which consists of porosity material in the continuation mold single reaction container shown in drawing 2 using the metal catalyst about the 2nd invention, and heating single storage tank B containing a hydrogenation aromatic compound to predetermined temperature with Heater J near the boiling point temperature of a hydrogenation aromatic compound -- setting -- evaporating -- warming -- a steam is introduced into the dehydrogenation catalyst reactor D through the side-face pipe E which is a means to supply a hydrogenation aromatic compound and/or an aromatic compound to the dehydrogenation catalyst reactor D equipped with the heater and the dehydrogenation catalyst. In the cooling condensation section C (for example, 10 degrees C), the steam of an aromatic compound and/or a hydrogenation aromatic compound is condensed, and it falls as a drop, and is dropped at the catalytic-reaction section A, and liquid membrane is formed. In the reaction temperature (180 degrees C) in this liquid membrane condition, a hydrogenation aromatic compound is efficiently changed into an aromatic compound, and generates hydrogen.

[0026] The aromatic compound and/or hydrogenation aromatic compound which became liquefied voice pass the inside of the catalytic-reaction section A, and a porosity material (K) container wall, and form the

liquid phase. Through the side-face pipe F as a means to lead a dehydrogenation product to said storage tank connected to the same location (height) as the catalyst bed of the catalytic-reaction section, a liquid phase aromatic compound and/or a hydrogenation aromatic compound flow into single storage tank B by the principle of a siphon, the always same location (height) as a catalyst bed is maintained, the oil level of an aromatic compound and/or a hydrogenation aromatic compound is formed, and desirable liquid membrane is secured to the catalytic-reaction section.

[0027] Vapor liquid separation is realized before and behind the cooling condensation section C, when only the big hydrogen gas of diffusion movement opens the outlet bulb H through the up pipe hydrogen decollator G light again in mass, separation purification of the high grade hydrogen is carried out, and, thereby, hydrogen is efficiently supplied to the object for residences, and an automotive fuel cell. In the case of storage of hydrogen, the hydrogen which controlled the power generated by the exposure of sunlight using the semi-conductor panel plate (amorphous silicon agent) attached in the lateral part of a residence thru/or an automobile, and was generated in the electrolysis-of-water tub can be introduced. The hydrogen gas of a high grade is introduced in catalytic-reaction equipment D by closing Bulb H and opening Bulb I. An aromatic compound is efficiently changed into a hydrogenation aromatic compound according to the support metal catalyst with which the catalytic-reaction section A heated by predetermined temperature was filled up, and, thereby, storage of hydrogen is made. The mixed liquor of benzene and the changed cyclohexane holding a liquid membrane condition according to the siphon effectiveness of the side-face pipe F, it is collected by storage tank B, and the aromatic compound thru/or hydrogenation aromatic compound of storage tank B evaporates, and is introduced into the reaction container D through the side-face pipe F. It cools by the cooling condensation section C, and is condensed, and it is dropped on the catalyst included in the catalytic-reaction section A, a hydrogenation reaction advances again, and the invert ratio of a hydrogenation aromatic compound [an aromatic compound thru/or] of a hydrogenation reaction improves further. This is followed in the hydrogenation reaction and dehydrogenation of an aromatic compound and a hydrogenation aromatic compound, it realizes in a single reaction container, and storage and the distribution system of hydrogen can be offered.

[0028] When the bulb which enables supply of the hydrogen to a dehydrogenation catalyst reactor is prepared, since the reverse reaction of a dehydrogenation advances and it becomes convertible into a hydrogenation aromatic compound about the aromatic compound in a storage tank, it is desirable by supplying hydrogen from this bulb.

[0029] In applying to a fuel cell powered vehicle or the fuel cell for a home generation of electrical energy, this system has low operating temperature and its fuel cell of the solid-state macromolecule mold which is a small light weight is desirable.

[0030] this invention person etc. considered optimization of the hydrogen storage using hydrogenation and dehydrogenation of an aromatic compound, and efficient actuation of a distribution system, and amelioration of the catalyst engine performance using the continuous system single reaction container of the above-mentioned invention, and searched for continuation mold hydrogenation and dehydrogenation conditions.

[0031] first , although not restricted to the diameter , the height , and the configuration of the tubed container K which consist of a porosity material of the catalytic reaction section A , the quality of the material of a porosity (filter) ingredient be understood that it be desirable that a receipts and payments of liquid with the outer case section , diffusion , etc. be optimize so that the liquid membrane formation of thermal resistance , such as a silica , an alumina , and an activated carbon fibrous , the aromatic compound in a catalyst bed , and a hydrogenation aromatic compound may be realize .

[0032] Sufficient thing for steam-izing for which it warms and the side-face pipe E is kept warm is desirable. As for the side-face pipe F, it is desirable to be set up so that the liquid column of an aromatic compound and a hydrogenation aromatic compound may be comparatively realized at low temperature. Although the cooling condensation section C is structure which contains the up container wall of the dehydrogenation catalyst reactor D fundamentally, in order to maintain things for which it has a heat exchanger and vapor liquid separation with an aromatic compound with generating hydrogen and a hydrogenation aromatic compound is realized efficiently, such as spiral capillary and mutual cooling pipe structure, and the liquid membrane condition of the catalyst bed in the catalytic-reaction section A, it is desirable to adjust and carry out the cooling water (for example, 5-20 degrees C) of optimum temperature.

[0033] Substantially, although it is possible by taking into consideration various-causes children, such as a touch area of the cooling condensation section C, a circulating water temperature, and generating hydrogen temperature, separation of hydrogen and the actuation means of purification are further realized by installing

the hydrogen decollators G by the conventional technique, such as a silica demarcation membrane, and palladium, a silver demarcation membrane, when supply of the high grade hydrogen more than a high grade (99.9%) is the need. It is not this limitation although it is common to set up fundamentally the stores dept. B of an aromatic compound and/or a hydrogenation aromatic compound near [those] the boiling point, and to be set as low temperature from the catalytic-reaction section A in comparison. It is not this limitation although the hydrogenation reaction of the aromatic compound in the process of hydrogen storage is generally performed with ordinary pressure - 10 atmospheric pressure in many cases.

[0034] In order to raise the hydrogen storage for the object for residences, and automobiles, and the effectiveness of supply, the support metal catalyst used as a catalyst was examined. Although a precious metal catalyst, for example, a carbon support platinum catalyst, is generally effective in the hydrogenation reaction and dehydrogenation of an aromatic compound If metal salts, such as iridium, a ruthenium, a rhenium, molybdenum, and a tungsten, are added to this and hydrogen reduction processing is performed to it recently, the catalyst engine performance will improve, Serially moreover, by adding the carbonyl complex supported as a metallic material, an acetylacetone salt, a cyclopentadienyl complex, etc. at coincidence or the carbon support platinum catalyst which is a main catalyst metal at a target, and performing hydrogen reduction processing after thermal decomposition It turned out that hydrogen storage and hydrogen supply effectiveness are furthermore improved.

[0035]

[Effect of the Invention] According to the system of the 1st invention, the hydrogen of a high grade can be easily supplied to a fuel cell.

[0036] The hydrogenation reaction and dehydrogenation of the bottom aromatic compound of existence of the metal catalyst of high performance can be made to advance efficiently using the continuation mold single reaction container of the 2nd invention, it is possible to realize storage and supply of hydrogen in a single reaction container continuously, and, thereby, an automobile, and the solid fuel cell hydrogen storage and the distribution system for a home generation of electrical energy can be maintained in the condition good for a long time.

[0037]

[Example] Hereafter, this invention is explained more to a detail using an example and the example of a comparison.

After being immersed in mezzo-soprano pore porosity material (FSM-16, SiO₂/aluminum₂O₃=300, 27.5Å of pore size), and surface area 970m²/g30g using the water solution and carrying out evaporation to dryness of the 3.3g of the example 1 chloroplatinic acid at 110 degrees C for 24 hours, evacuation was performed at 320 degrees C for 2 hours, and the platinum active ingredient (1) was prepared 5%. Using this catalyst, dehydrogenation of a cyclohexane was performed in the following way and the invert ratio and hydrogen generating rate of a cyclohexane were measured. The catalytic-reaction section A was filled up with the catalyst, and it returned at 300 degrees C among the hydrogen air current for 1 hour.

[0038] After it put 27ml cyclohexane into the stores dept. B and the high grade argon permuted the inside of a reaction container, when the stores dept. B was warmed at 90 degrees C, and the catalytic-reaction section A was warmed at 180 degrees C and water cooling (pump) of the cooling condensation section C was carried out to 10 degrees C, hydrogen generation began after 20 minutes, the initial hydrogen generation rate of 30 minutes [per hour] after was per-hour 12.0L, and the invert ratio to the benzene of a cyclohexane was 25%.

[0039] moreover, instead of [of a cyclohexane] -- benzene 27ml -- a stores dept. B -- putting in -- the catalytic-reaction section A -- a catalyst (1) -- the hydrogenation reaction of vane ZEN was similarly performed under the reaction temperature of 200 degrees C, and 1 atmospheric-pressure hydrogen after 300-degree-C 2-hour reduction by the hydrogen air current. The resultant was only a cyclohexane. Moreover, it was 52% 18% of initial invert ratios of benzene, and 5 hours after.

Using a conventional-type fixed-bed gaseous-phase circulation type reactor (the reactor made from SUS with a bore of 1.8cm being filled up with Catalyst A) as an example of comparison 1 reaction container, it circulated and cyclohexane vapor pressure (90 degrees C) was performed with the reaction temperature of 180 degrees C. The cyclohexane invert ratio of SV=1500 ml/gcat / hydrogen generation rate was 1.6% in per hour 0.8 L. Little detection of the methane which is the decomposition product of a cyclohexane a part, n-hexane, a propane, and the ethane was carried out.

After filling up the conventional-type standing type autoclave (an SUS box-manufacturing-like container, volume of 150ml) with 30g of catalysts A as an example of comparison 2 reaction container and performing 2h of bottom 250-degree-C reduction of H₂, the cyclohexane was introduced and it reacted by heating at

180 degrees C. The resultant was analyzed at 180 degrees C, performing internal stirring in the state of suspension. The generation rate of hydrogen was 0.35ml and the invert ratio of a cyclohexane was 0.85%. After being immersed in activated carbon 3200m²/g and alkali treatment using the water solution of 3.3g of example 2 chloroplatinic acid, it dried at 110 degrees C among air for 15 hours. It returned at 350 degrees C in H₂ air current, and the activated carbon support catalyst B was acquired 5%. these catalysts B and Ir₄(CO)₁₂ and Mo(CO)₆ and Ru₃(CO)₁₂ and Re₂(CO) -- ten -- every -- dehydrogenation of a cyclohexane was performed, after having adjusted to Pt/M=2-1 (M=Ir, MoRu, Re), mixing among the argon air current and heating at 180 degrees C - 200 degrees C from a room temperature. The reaction condition and the reaction property were the same, and performed the example 1. The resultant was only benzene. The initial hydrogen generation rate reached and showed the invert ratio to the cyclohexane of 2 hours after in Table 1. Analysis of a product is porapak by the gas-chromatograph method. Quality and quantitative analysis were carried out by the FID gas chromatograph (Shimazu 8A) using P.

The hydrogenation reaction of benzene was performed for the catalyst A acquired in example 3 example 1 by the respectively same reaction condition and the operation information as the example 2 after 350-degree-C 2-hour hydrogen reduction in a hydrogen air current. A product is only a cyclohexane.

In reaction temperature (reaction section A temperature of 210 degrees C) and the stores dept. B temperature of 215 degrees C, and 10 degrees-C cooling of condensation sections, it carried out using decalin 10ml using catalyst B-2.5g prepared in the example 4 example 2. The hydrogen generation rate and the decalin invert ratio were shown in Table 2.

[0040]

[Table 1]

シクロヘキサン脱水素反応での水素生成活性

触媒	M/P t	水素生成速度 (L/h)	シクロヘキサン 転化率(%)
Pt/C	0	16.0	20
Pt-Ir/C	5	46.4	58
Pt-Re/C	3	22.4	28
Pt-Mo/C	4	28.0	35
Pt-W/C	5	36.0	45
Pt-Ru/C	8	20.0	25

[0041]

[Table 2]

デカリン脱水素反応での水素生成活性

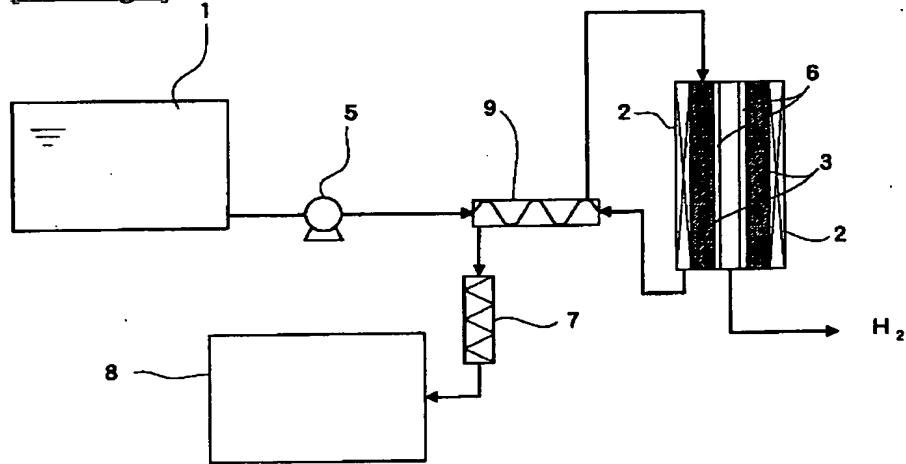
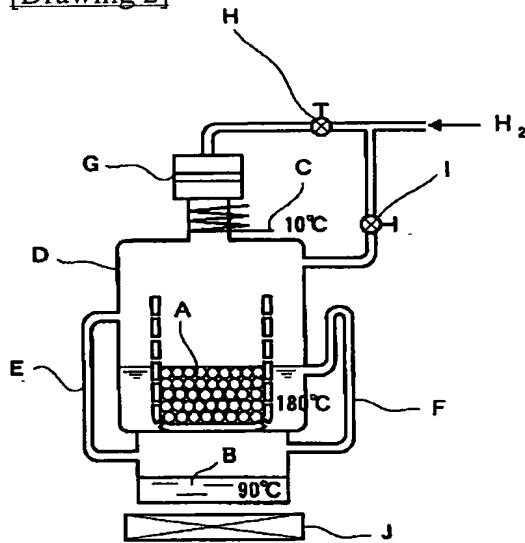
触媒	M/P t	水素生成速度 (L/h)	シクロヘキサン 転化率(%)
Pt/C	0	3.8	18
Pt-Re/C	3	4.6	22
Pt-Ru/C	8	4.2	20
Pt-W/C	5	5.7	27
Pt-Ir/C	4	7.7	36

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DRAWINGS**[Drawing 1]****[Drawing 2]**

[Translation done.]

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